PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Form PCT/IPEA/416
JTS/P13455PC		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB2005/001169	24.03.2005	26.03.2004

International Patent Classification (IPC) or national classification and IPC
INV. C25B1/06

Applicant
THE UNIVERSITY COURT OF THE UNIVERSITY OF ST. ANDR

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 3 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in celectronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
20.01.2006	13.04.2006

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/GB2005/001169

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-19	as originally filed
Claims, Numbers	
1-18	received on 30.01.2006 with letter of 20.01.2006
Drawings, Sheets	
1/4-4/4	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	5,7-18
	No:	Claims	1-4,6
Inventive step (IS)	Yes:	Claims	13,14
	No:	Claims	5,7-12,15-18
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Cited documents

Reference is made to the following documents, in particular to those passages mentioned in the search report:

D1: IWAHARA H: "Technological challenges in the application of proton conducting ceramics" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 77, April 1995 (1995-04), pages 289-298, XP004050460 ISSN: 0167-2738

D2: EP-A-0 472 922 (FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V) 4 March 1992 (1992-03-04)

D3: SCHNELLER T ET AL: "Chemical solution deposition prepared dense proton conducting Y-doped BaZrO3 thin films for SOFC and sensor devices" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 164, no. 3-4, November 2003 (2003-11), pages 131-136, XP004473999 ISSN: 0167-2738

D4: IWAHARA H ET AL: "PROTON CONDUCTION IN SINTERED OXIDES BASED ON BACEO3" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 135, no. 2, 1 February 1988 (1988-02-01), pages 529-533, XP000073186 ISSN: 0013-4651

D5: VALKENBERG S ET AL: "The electrical conductivity of the high temperature proton conductor Ba3Ca1.18Nb1.82O9-delta" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 97, no. 1-4, 1 May 1997 (1997-05-01), pages 511-515, XP004126222 ISSN: 0167-2738.

Novelty, Article 33(2) PCT

The independent claims 1 and 3 of the present application define a porous or gas permeable substrate which according to claim 1 is redox stable and coupled to an anode for connection to the positive pole. Claim 4 defines that "the substrate material is electrochemically active and the anode constitutes part of the substrate" and the description at page 2, lines 22-25 states that "in the simplest case the anode may simply form part of the substrate".
It follows from these statements that the anode is not to be considered a separate device or layer, unless defined otherwise (e.g. in dependent claim 5).

D1 discloses a steam electrolyzer comprising a porous anode, a porous cathode and a perovskite electrolyte.

The subject-matter of claims 1-4 and 6 is therefore not new over D1.

Inventivity, Article 33(3) PCT

The additional features of dependent claims 5, 7-12 and 14-18 are not directed towards inventive subject-matter for the following reasons.

Claims 5, 17, 18 concern features of a porous substrate on which the anode of a steam electrolyzer is applied. The problem solved may be regarded as providing a supported cell. This problem is solved by D2 which is directed towards a reversible fuel cell which comprises a sintered substrate of e.g. titanium, niobium and a cation exchange membrane coated on both sides with an electrocatalyst.

Claims 7 and 11 concern alternative perovskite proton conductive materials. Such materials are suggested by documents D3 ($BaZrO_3$-based materials), D4 ($BaCeO_3$-based materials) and D5 (BCN18) for use in steam electrolyzers. It is therefore obvious to use these materials in a steam electrolyzer cell known from D1.

Claims 8-10 and 12 are directed towards features of the proton conductive membrane which come within the routine of a person skilled in the art.

Claims 15 and 16 concern features of the substrate support. The substrates are routinely used in the art of fuel cells and therefore not considered inventive.

The particular proton conductive material of claims 13 and 14 is not suggested as electrolyte for steam electrolysis by the prior art.
Claims 13 and 14 therefore meet the requirements of Article 33(1) PCT for novelty and inventivity.

CLAIMS

(42)

1. A method of producing hydrogen comprising: providing a steam feed stream at one side of a porous redox stable substrate, contacting said steam feed stream with a proton conducting membrane supported on the other side of said porous redox stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a cathode coupled to the other side of said membrane so as to dissociate at least part of said steam feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.

2. A method as claimed in claim 1 wherein steam electrolysis is carried out at a temperature of from 400 to 800°C.

3. A steam electrolyser apparatus for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

4. An apparatus as claimed in claim 3 wherein the

substrate material is electrochemically active and the anode constitutes part of the substrate adjoining the membrane.

5. An apparatus as claimed in claim 3 wherein the anode comprises a thin layer of a different material interposed between the membrane and the substrate support.

6. Apparatus as claimed in any one of claims 3 to 5 wherein the proton conducting membrane is often oxygen deficient perovskite of formula $ABO_{3-\delta}$ wherein A and B represent metallic elements occupying the A and B sites of the perovskite lattice structure and δ represents the degree of oxygen deficiency.

7. Apparatus as claimed in claim 6 wherein said membrane material is selected from $BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY10), $BaZr_{0.9}Y_{0.1}O_{2.95}$ (BZY) and members of the solid solution, $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$ (BCZY), or the analogues of the previously mentioned phases with lanthanides such as Gd, Nd or Yb instead of Y and such phases with higher degrees of substitution such as $BaCe_{0.8}Y_{0.2}O_{2.95}$ (BCY20), $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$ (SCZTO) and $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$ (BCN18) composites of such materials.

8. Apparatus as claimed in any one of claims 3 to 7 wherein the membrane is provided with an outer protective layer.

9. Apparatus as claimed in any one of claim 3 to 8 wherein the membrane thickness is not more than 25μm.

10. Apparatus as claimed in claim 9 wherein the membrane thickness is from 3 to 15μm.

11. Apparatus as claimed in any one of claims 3 to 10 wherein the membrane comprises a $BaZrO_3$-based material.

12. Apparatus as claimed in claim 11 wherein said $BaZrO_3$ based material is prepared with the use of a sintering aid.

13. Apparatus as claimed in claim 12 wherein the membrane is of $BaZr_{1-x}Ln_xO_{3-x/2}$ wherein X has a value in the range from (0.02) to (0.25) and Ln is a lanthanide ion or La,Y,Sc, and wherein said membrane is produced with the use of approximately 1% w/w of ZnO sintering aid.

14. Apparatus as claimed in claim 12 wherein the membrane is of $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{2.88}$.

15. Apparatus as claimed in any one of claims 3 to 14, wherein the substrate support is of a material which comprises a metallised ceramic or a mixed conductive oxide, having an electrical conductivity of not less than $10Scm^{-1}$ at the operating temperature of the steam electrolysis.

16. Apparatus as claimed in claim 15 wherein said substrate material is selected from $Cu:Al_sO_3$, $La_{0.8}Sr_{0.2}MnO_3$ (LSM), chromium-doped LSM (i.e. $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF).

17. Apparatus as claimed in any one of claims 3 to 16 wherein the substrate support pore size is not less than 0.5 μm.

18. Apparatus as claimed in any one of claims 3 to 17 wherein the substrate porosity is from 30 to 60%.